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(54) Title: METHOD FOR FABRICATING MULTI-METALLIC HYDROGEN OXIDATION ELECTROCATALYST MATERIALS

(57) Abstract: The invention provides a process for fabricating supported or unsupported multimetallic catalysts and uses thereof.



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METHOD FOR FABRICATING MULTI-METALLIC HYDROGEN OXIDATION ELECTROCATALYST MATERIALS

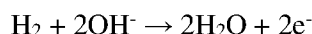
TECHNOLOGICAL FIELD

The invention generally concerns methods for fabricating multi-metallic hydrogen oxidation electrocatalyst materials from organometallic reagents.

BACKGROUND

A fuel cell uses the chemical energy of dihydrogen or another fuel to cleanly produce electricity. Fuel cells can operate at higher efficiencies than known combustion engines and can convert the chemical energy in the fuel to electrical energy with efficiencies of up to 60%.

The technology associated with anion exchange membrane fuel cells (AEMFC) has received significant interest in recent years, because it has the potential of overcoming cost barriers of polymer electrolyte fuel cells, as the basic environment of the anion exchange membranes allows the use of less expensive electrocatalysts and low-cost metal hardware. The electrocatalysts are used as cathode and anode materials. In the latter case, the anode electrocatalyst catalyzes the oxidation of the fuel, which is dihydrogen, according to the reaction:



International Patent Application no. WO 2013/184269 [1] discloses the use of bi-metallic systems as anode electrocatalyst, where at least one metal is active towards dihydrogen oxidation and at least one metal is oxophilic, i.e. spontaneously forms surface hydroxide in the conditions of operations of the AEMFC. A special attention has been drawn to nickel-palladium anode catalysts.

In a previous study [2], the highest performance for an AEMFC was obtained when using Pt-free catalysts, the performance reaching 400 mW/cm² peak power. The catalyst was prepared by deposition of Pd on Ni utilizing an aqueous method.

Several synthetic routes are known for the preparation of Ni/Pd nanoparticles (NPs), some of which lead to Ni@Pd or Pd@Ni core/shell morphologies while others to

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a PdNi alloy, depending on the precursors, reaction conditions, and the addition sequence of the reagents.

The use of organometallic precursors has been reported for the synthesis of alloyed NPs of Pd-Ni, used as catalysts for hydrogenation [3] and methanol electro-oxidation [4]. In both cases, the catalytic activity was similar to the catalysts produced by a standard method [5].

REFERENCES

- [1] WO 2013/184269;
- [2] Journal of Power Sources, 304, 332-339 (2016);
- [3] ACS Catal., 4, 1735–1742 (2014);
- [4] J. Nanopart. Res., 17, 474 (2015);
- [5] International Journal of Hydrogen Energy, 41, 19556-19569 (2016).

SUMMARY OF THE INVENTION

The invention subject of the present application relates to a one-pot or a one-step synthesis of multimetallic catalysts from organometallic reagents, e.g., utilizing two or more organometallic compounds, to yield bi-metallic or multimetallic electrocatalysts, depending on the number of metals used. These electrocatalysts display higher activities than those synthesized by other synthetic routes reported to date.

The multimetallic catalysts are composed of two or more metals, e.g., bimetallic catalysts, and are obtained from the corresponding organometallic precursors. In other words, each of the two or more metals making-up a catalyst of the invention is derived from an organometallic precursor. In accordance with the process of the invention, the organometallic precursors (reagents) of metals described herein, are reacted in one-pot, in a reaction sequence, under conditions of thermal activation or by chemical activation.

In one of its aspects, the invention provides a one-pot process enabling preparation of supported or unsupported multimetallic catalysts, e.g., bimetallic catalysts (such as NiPd and FePd), the process comprising sequentially adding at least one organometallic precursor of one metal (e.g., being a precursor of metal 1) and at least one organometallic precursor of another metal (e.g., being a precursor of metal 2), and optionally at least one organometallic precursor of a further metal (e.g., being a precursor of metal 3 or further), and permitting said organometallic precursors to form

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into nanoparticles comprising two or more metals (e.g., metals 1, 2 and optionally 3). In a similar fashion, precursors of further and different metals may be added to form a multimetallic electrocatalyst.

In some embodiments, one or more metal precursors of a single metal may be used. For example, two different precursors of metal 1 may be used.

In some embodiments, the precursor form of two or more of the metals may be the same or different.

In some embodiments, all metals used in a reaction are different, namely metals 1 and 2 and 3 and any additional metal(s) are different from each other.

In some embodiments, the number of metals used is two, thus providing a bimetallic electrocatalyst. In some embodiments, the number of metals used is three, thus providing a tri-metallic electrocatalyst. In other embodiments, a larger number of metals may be used, affording a great variety of multimetallic electrocatalysts, paving the way for controlled construction of specific catalysts exhibiting tailored improved characteristics.

In some embodiments, one metal is a catalytically active metal and one or more of the other metals (e.g., another and/or the further metal) is at least one catalytically active or inactive metal, as selected herein.

Without limitation, the catalytically active metal may be selected from ruthenium (Ru), Iridium (Ir), Palladium (Pd), Platinum (Pt), Rhodium (Rh), Osmium (Os) and Gold (Au) whereas the catalytically inactive metal may be selected from Titanium (Ti), Vanadium (V), Chromium (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Lanthanum (La) and Cerium (Ce).

In some embodiments, the catalytically active metal is Pd.

In some embodiments, the catalytically inactive metal is Ni, Fe or Co.

The at least one Pd organometallic precursor is bis(dibenzylideneacetone) palladium(0), $(\text{Pd}(\text{dba})_2)$, $\text{Pd}_2(\text{dba})_3$ or any Pd(0) organometallic compound.

As used herein, the at least one Ni organometallic precursor is bis(1,5-cyclooctadiene) nickel(0), $(\text{Ni}(\text{COD})_2)$, $\text{Ni}(\text{CO})_4$, nickelocene or any Ni organometallic compound.

The at least one Fe organometallic precursor is iron pentacarbonyl ($\text{Fe}(\text{CO})_5$), or any other Fe organometallic material.

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The ratio between the two precursors (and similarly between any two in a combination of three or more precursors) is between 1:1 and 1:10 or between 1:1 and 10:1, e.g., Pd:Ni %w/w. In some embodiments, the ratio is 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1, e.g., Pd:Ni, % w/w.

In some embodiments, the ratio between a catalytically active precursor and a catalytically inactive precursor is between 1:1 and 1:10 or between 1:1 and 10:1 %w/w. In some embodiments, the ratio is 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1 % w/w.

The support material may be selected from any carbonaceous material or nanomaterial or any carbon allotrope. Such carbonaceous materials may be selected from activated carbon, graphite and graphitized materials, glass-like carbons, carbon black, carbon nanotubes (e.g., single-walled (SWCNTs) or multi-walled (MWCNTs)), carbon nanofibers, graphene and few-layer graphene, fullerenes and others.

The total metal loading on the carbonaceous material may be at least 20% up to 95%. In some embodiments, the loading is at most 95%.

In some embodiments, the support material may be in the form of metal powders (e.g., Ag, Ni, Cu, Co, Pd, Ru, Mo) of individual metals, as alloyed materials, in combination or in any form acceptable in the field, wherein material loading is at least 20% and up to 95%.

In accordance with the invention, the organometallics are reacted with each other in a single pot. For example, the at least one Ni organometallic precursor and at least one Pd organometallic precursor are added sequentially, namely, one after the other. In some embodiments, each of the at least one Ni organometallic precursor and at least one Pd organometallic precursor are pre-dissolved in at least one solvent which may be any one or more organic solvents. The organic solvent may be selected from aromatic solvents such as toluene, mesitylene, anisole, benzyl alcohol or alkyl ethers such as THF.

The addition onto the carbon or metallic material may be carried out while in solution, or in suspension.

The process may be carried out at room temperature (22-34°C) or at a temperature higher than 70°C. In some embodiments, the temperature is above 70°C, above 80°C, above 90°C, above 100°C, above 110°C, above 120°C, above 130°C, above 140°C, above 150°C or above 160°C.

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In some embodiments, the temperature is above 70°C and below 250°C.

In some embodiments, the process is carried out under microwave radiation, at room temperature or at a temperature above 70°C.

The reaction proceeds over a period of between 1-2 hours. The resulting NPs may be precipitated by centrifugation (11,000 rpm x 20 min) and washed 3 times with a mixture of ethanol:toluene (1:1) (11,000 rpm x 15min) and then with ethanol (11,000 rpm x 15min).

In some embodiments, the organometallic compound bis(1,5-cyclooctadiene)nickel(0), (Ni(COD)₂), is used as precursor for deposition on palladium (Pd) supported or unsupported catalysts.

In some embodiments, a palladium organometallic compound bis(dibenzylideneacetone)palladium(0), (Pd(dba)₂) or Pd₂(dba)₃ is reacted in a one-pot or sequential reaction with Ni(COD)₂ to form alloyed or core-shell catalysts, respectively. The carbon support can be carbon black, carbon nanotubes or graphene.

The method of the invention enables the fabrication of fine, well-dispersed catalyst materials, such as NiPd nanoparticles being 4.0-4.5 nm in diameter, which may be uniformly spread over the surface of a carbon support.

The invention further provides carbon supported NiPd alloy, obtained according to a method of the invention.

In some embodiments, the NiPd alloy is in the form of NPs ~ 4-4.5 nm NPs. In some embodiments, the Ni:Pd ratios are 30:70 or 70:30 % w/w and total metal loading is 50 or 40 % w/w.

The method of the invention further enables the formation of non-supported catalysts.

The invention further provides methods and materials for the fabrication of FePd, NiPd, or CoPd catalysts.

In accordance with the invention, the organometallic complexes can be used directly on the catalyst support, which can be a metallic or a carbon powder, for the preparation of anode catalysts with unprecedented activity. While several different materials have been developed and successfully tested as hydrogen oxidation reaction (HOR) catalysts in AEMFC (such as unsupported NiPd, C-supported NiPd, Ni supported on Pd, Pd supported on Ni, Ni supported on C/Pd, unsupported FePd, carbon

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supported FePd and Ag supported NiPd), in all cases the organometallic route of the invention led to higher HOR activity, namely superior electrocatalysis.

As noted above, the multimetallic catalysts may be based on pairs of metals, one of which being a catalytically active metal and the other a catalytically inactive component. Additional metals may be present. Without limitation, the catalytically active metal and the catalytically inactive metal may be selected from the metals discussed hereinabove.

In some embodiments, the catalytically active metal is Pd.

In some embodiments, the catalytically inactive metal is Ni, Fe or Co.

In another aspect, the invention provides an anode catalyst for alkaline HOR, wherein the catalytically active metal is palladium (Pd).

In another aspect, the invention provides an anode catalyst for alkaline HOR, wherein the catalytically inactive metal is Ni, Fe or Co.

In some embodiments, the anode catalyst is palladium (Pd) – nickel (Ni), palladium (Pd) – iron (Fe), or palladium (Pd) – cobalt (Co), each of which being in the form of nanomaterial.

In some embodiments, the following catalysts are provided:

1. Catalyst: C:Ni:Pd; Relative amounts: 60:12:28; Ratio Ni:Pd: 30:70
2. Catalyst: C:Ni:Pd; Relative amounts: 50:15:35; Ratio Ni:Pd: 30:70
3. Catalyst: C:Ni:Pd; Relative amounts: 60:28:12; Ratio Ni:Pd: 70:30
4. Catalyst: C:Ni:Pd; Relative amounts: 50:35:15; Ratio Ni:Pd: 70:30.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to better understand the subject matter that is disclosed herein and to exemplify how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

Figs. 1A-F show TEM images of carbon supported PdNi alloyed NPs.

Fig. 2 shows size distribution histograms of NiPd NPs obtained from evaluation of TEM images taking into account 200 nanoparticles.

Fig. 3 shows histograms of input and TEM/EDS elemental compositions.

Fig. 4 shows cathodic scans for the C/PdNi samples at 900 rpm.

Figs. 5A-B present the polarization curves (**Fig. 5A**) and power density curves (**Fig. 5B**) of bimetallic C/PdNi alloyed NPs.

Fig. 6 shows an HRTEM image of $\text{Ni}_2\text{O}_3\text{H}$ nanocrystals supported on Pd nanopowder. Inset: FFT analysis of the crystal in the white square (ZA: zone axis [-11-2]).

DETAILED DESCRIPTION OF EMBODIMENTS

1. Carbon Supported NiPd alloys by standard heating

The carbon supported NiPd alloyed nanoparticles (NPs) were prepared by the simultaneous decomposition of $\text{Ni}(\text{COD})_2$ and $\text{Pd}(\text{dba})_2$ onto a carbon substrate such as Vulcan-XC72 surface. The resulting NPs were characterized and electrochemically tested.

According to literature data, deposition of resulting metal NPs onto Vulcan XC-72 has been achieved in the last reaction stages. The significant improvement of the method is deposition of organometallic precursors onto the Vulcan-XC72 through a one-pot synthesis.

The inventors have developed reaction conditions (**Table 1**) which make it possible to obtain well dispersed Carbon/CNT supported NiPd alloys, ~ 4-4.5 nm NPs. C/NiPd NPd were prepared with various Ni:Pd ratios (30:70 or 70:30 % w/w) and total metal loading (50 or 40 % w/w). Furthermore, the influence of temperature (110-150°C) and reaction time (1-2 h) on the morphology, resulting stoichiometry and electrochemical activity (**Table 1**) were tested.

The Vulcan-XC72 was dispersed in mesitylene (100 mL) at 110-150°C for 1-2 h under N_2 atmosphere and continuous stirring.

In a glovebox, $\text{Ni}(\text{COD})_2$ and $\text{Pd}(\text{dba})_2$ were dissolved in dry Toluene (~ 40 mL for each precursor). Subsequently, the solutions were sequentially introduced into the Vulcan-XC72 suspension, one after the other. The reaction proceeded for 1-2 hours. The resulting NPs were precipitated by centrifugation (11,000 rpm x 20 min) and washed 3 times with a mixture of ethanol:toluene (1:1) (11,000 rpm x 15min) and then with ethanol (11,000 rpm x 15min).

The NPs were dried at 70°C for 24 h and finally at 150°C for 4 h, under high vacuum in order to remove residues of organic materials.

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	Vulcan, mg	Ni(COD) ₂ , mg	Pd(dba) ₂ , mg	T °C/t h
Sample: MA-133 Catalyst: C:Ni:Pd Relative amounts: 60:12:28 Ratio Ni:Pd: 30:70	120	112.46	302.54	150/1h
Sample: MA-134 Catalyst: C:Ni:Pd Relative amounts: 50:15:35 Ratio Ni:Pd: 30:70	100	140.58	378.17	110/1.5 h
Sample: MA-135 Catalyst: C:Ni:Pd Relative amounts: 60:28:12 Ratio Ni:Pd: 70:30	120	262.42	129.66	110/2h
Sample: MA-136 Catalyst: C:Ni:Pd Ratio Ni:Pd: 70:30 Relative amounts: 50:35:15	100	328.02	162.07	120/2h
Sample: MA-137 Catalyst: C:Ni:Pd Relative amounts: 60:12:28 Ratio Ni:Pd: 30:70	120	112.46	302.54	110/1h

Table 1: Reaction conditions and reagent quantities

2. Preparation of C/NiPd by microwave technique

In a glovebox, Ni(COD)₂ (112.5 mg) and Pd(acac)₂ (160,4 mg) were dissolved in dry Benzyl Alcohol (~ 15 mL for each precursor). The Vulcan-XC72 (120 mg) was dispersed in dry Benzyl Alcohol (~15 mL) with constant magnetic stirring. Afterward, the precursor's solutions and Vulcan-XC72 suspension were sequentially introduced into the pressure tube, one after the other. The reaction mixture was transferred to microwave oven and heated at 170°C (run time 2 min, hold time 10 min). The products were separated from reaction medium via centrifugation (11,000 rpm x 20 min) and

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washed 3 times with a mixture of ethanol: toluene (1:1) (11,000 rpm x 15min) and then with ethanol (11,000 rpm x 15min).

The NPs were dried at 70°C for 24 h and finally at 150°C for 4 h, under high vacuum in order to remove residues of organic materials.

3. Nickel supported onto C/Pd

In a glovebox, Ni(COD)₂ (234 mg) was dissolved in dry THF (~ 60 mL) and then C/Pd 20 % w/w (400 mg) was added. To the reaction was allowed to continue under constant stirring overnight. At the end, the products were separated from reaction medium via centrifugation (11,000 rpm x 20 min) and washed 3 times with THF (3.500 rpm x 15min).

4. Preparation of C/FePd

The Vulcan-XC72 (300 mg) was dispersed in mesitylene (150 mL) at 70°C for 1 h under N₂ atmosphere and continuous stirring.

In a glovebox, Pd(dba)₂ (420 mg) were dissolved in dry Toluene (~ 40 mL) and Fe(CO)₅ 237 µL was dissolved in dry Toluene (~ 3 mL). Subsequently, the solutions were sequentially introduced into the Vulcan-XC72 suspension, one after the other and the temperature was raised to 150°C. The reaction proceeded 2 hours. The products were separated from reaction medium via centrifugation (11,000 rpm x 20 min) and washed 3 times with a mixture of ethanol:toluene (1:1) (11,000 rpm x 15min) and then with ethanol (11,000 rpm x 15min).

The NPs were dried at 70°C for 24 h and finally at 150°C for 5 h, under Ar/H₂ atmosphere in order to improve a Fe/Pd catalytic activity.

5. Nickel supported onto Pd

In a glovebox, Ni(COD)₂ (234 mg) was dissolved in dry toluene (~ 60 mL) and then Pd nanopowder (400 mg) was added. The reaction was allowed to stir for one hour at 110 °C. At the end, the products were separated from reaction medium via centrifugation (11,000 rpm x 20 min) and washed 3 times with a mixture of ethanol: toluene (1:1) (11,000 rpm x 15min) and then with ethanol (11,000 rpm x 15min).

5.2 Characterization

5.3 TEM

Figs. 1A-F present TEM images of C/NiPd NPs prepared according to **Table 1** (**Fig. 1F** shows scaling up of MA-135). These images reveal very highly dispersive NiPd alloys on the Vulcan surface, in all samples. It is important to note that the range of reaction conditions did not have an impact on the morphology and size distribution of nanoparticles (**Fig. 2**).

The method of the invention achieves an excellent control on the stoichiometry of elements. **Fig. 3** shows input ratios/output ratios of NiPd NPs based on TEM/EDS results.

Nickel supported on Pd or C/Pd has been characterized by HRTEM, the reaction yields a specific phase $\text{Ni}_2\text{O}_3\text{H}$ (**Fig. 6**).

5.4 Electrochemical Tests

The electrochemical measurements were collected in a polypropylene cell in a three-electrode configuration, with a polished 0.196 cm^2 glassy carbon disk as a working electrode, glassy carbon rod as a counter electrode and a reversible hydrogen electrode (RHE) as a reference electrode.

The catalyst loading on the glassy electrode was $5 \mu\text{g cm}^{-2}$. The alkaline aqueous solution was prepared from KOH (Sigma-Aldrich, 99.998%) and ultrapure water. The glassy carbon was mounted on a rotating electrode (Pine instruments) and all the data was collected with a VMP3 potentiostat (Bio-Logic). Potentials were corrected for ohmic losses, measured by impedance spectroscopy before each polarization curve. All gases were used with the highest purity available (99.999%).

After a purge in Ar for 15 min, the voltammogram was collected at 50 or 100 mV s^{-1} after stabilization for 50 cycles from 0.05 to 1.3 or 1.5 V vs RHE. The polarization curves were recorded after saturation of the solutions with H_2 by sweeping from OCV to 1 V vs RHE (positive going scan) and back (negative going scan) at 5 mV s^{-1} and 900 rpm).

Table 2 summarizes electrochemical data and TEM/EDS measurements. The quantities of materials (Pd, Ni and C, in μg) have been calculated on the basis of the data from TEM/EDS.

The HOR catalytic activity was assessed by evaluation of the surface area using the cyclic voltammetry (CV). Pd and Ni surface areas (cm^2) were calculated from the anodic peaks at ~ 600 mV and 1300 mV vs. RHE using 424 mC/cm^2 and 514 mC/cm^2 charges, respectively (Table 2).

sample	Pd, μg	Ni, μg	Carbon, μg	Pd surf cm^2	Ni surf cm^2	Pd:Ni	0.1V $(\text{mA/mg}_{\text{Pd}})$	0.1V $(\text{mA/cm}^2 \text{ mg}_{\text{Pd}})$
MA-133	1.33	0.52	3.15	0.115	0.299	28:72	15	75
MA-134	2.04	0.49	2.47	0.536	0.514	51:49	34	174
MA-135	0.82	1.55	2.62	0.310	2.095	13:87	146	696
MA-136	0.92	1.56	2.51	0.183	0.981	16:84	89	454
MA-137	1.58	0.46	2.96	0.315	0.297	51:49	33	157
MA-143	0.6	1.4	3.01	0.221	1	18:82	200	1050

Table 2: Summary of electrochemical measurements

For the purpose of evaluating the activity of different catalysts, the polarization curves (900 rpm) were normalized with respect to both surface area (specific activity, $\text{mA/cm}^2_{\text{Pd}}$) and loading amount of Pd (mass activity, mA/mg_{Pd}).

Samples MA-135 and MA-136 with high nickel content (Ni:Pd 70:30) exhibited higher specific activities and mass activities at 0.1V vs. RHE (Table 2, Fig. 4). This may be attributed to the synergistic interaction between the oxophilic surface of Ni and Pd.

The MA-135 sample was selected for scaling up for testing in AEMFC. Fig. 5 shows results of polarization and power density curves of bimetallic C/PdNi NPs. The Pd loading on electrode was 0.1 mg/cm^2 . The current density at 0.6 V is 0.7 A cm^{-2} . The peak power density was obtained at $\sim 600 \text{ mW/cm}^2$.

CLAIMS:

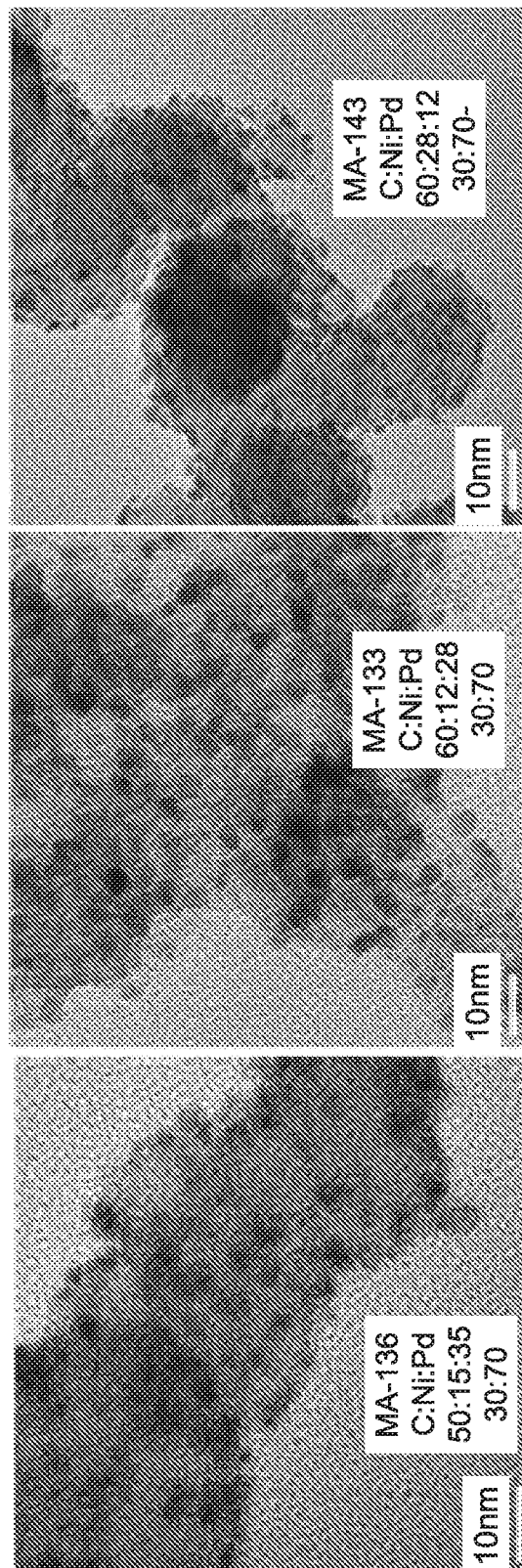
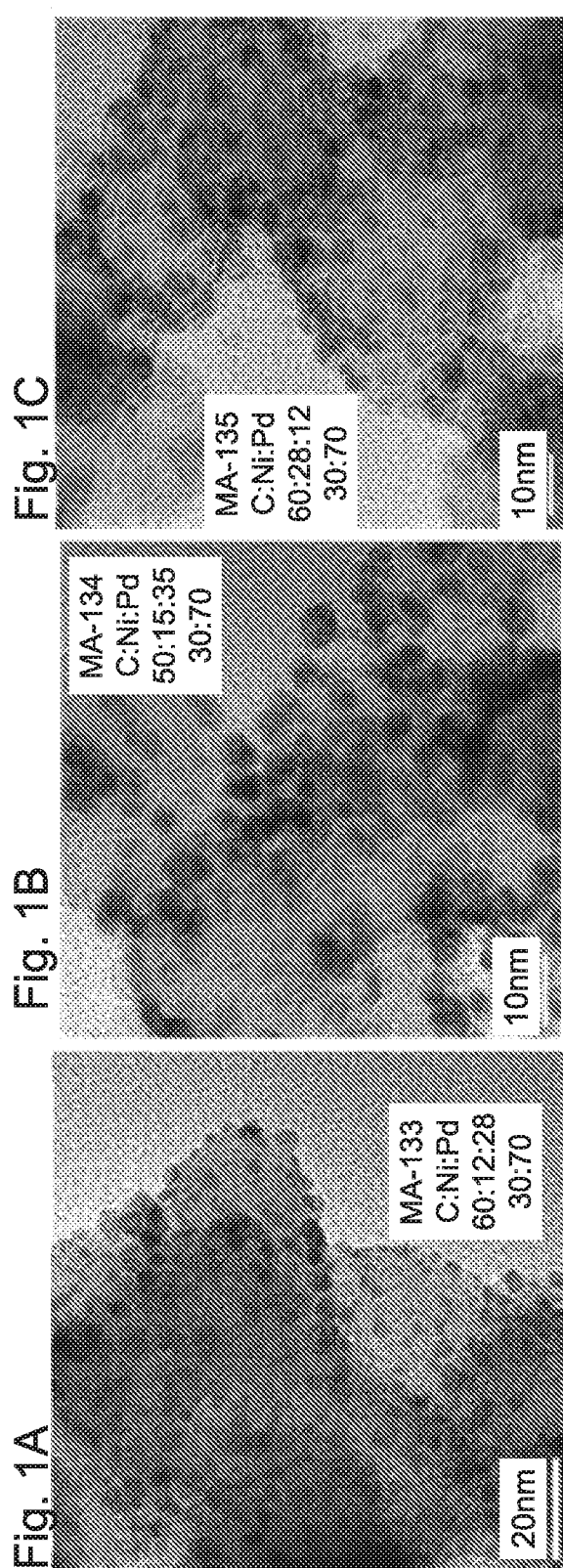
1. A process for fabricating a supported or an unsupported multimetallic catalyst, the process comprising reacting at least one organometallic precursor of one metal, at least one organometallic precursor of another metal, and optionally at least one organometallic precursor of a further metal under conditions permitting said organometallic precursors to form into nanoparticles comprising two or more metals.
2. The process according to claim 1, wherein the one metal is a catalytically active metal and the another metal and/or the further metal is at least one catalytically active or inactive metal.
3. The process according to claim 1 or 2, wherein at least one of said one metal, another metal and a further metal is catalytically active and at least another of said one metal, another metal and a further metal is catalytically inactive.
4. The process according to claim 2 or 3, wherein the catalytically active metal is selected from ruthenium (Ru), Iridium (Ir), Palladium (Pd), Platinum (Pt), Rhodium (Rh), Osmium (Os) and Gold (Au).
5. The process according to claim 2 or 3, wherein the catalytically inactive metal is selected from Titanium (Ti), Vanadium (V), Chromium (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Lanthanum (La) and Cerium (Ce).
6. The process according to claim 2 or 3, wherein the catalytically active metal is Pd.
7. The process according to claim 2 or 3, wherein the catalytically inactive metal is Ni, Fe or Co.
8. The process according to claim 1, wherein the at least one organometallic precursor of the one metal, another metal or the further metal is of Pd.
9. The process according to claim 8, wherein the at least one organometallic is bis(dibenzylideneacetone)palladium(0), $\text{Pd}(\text{dba})_2$ or $\text{Pd}_2(\text{dba})_3$.
10. The process according to claim 1, wherein the at least one organometallic precursor of the one metal, another metal or the further metal is of Ni.
11. The process according to claim 10, wherein the at least one organometallic precursor of Ni is bis(1,5-cyclooctadiene) nickel(0) $\text{Ni}(\text{COD})_2$, $\text{Ni}(\text{CO})_4$ or nickelocene.

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12. The process according to claim 1, wherein the at least one organometallic precursor the one metal, another metal or the further metal is of Fe.
13. The process according to claim 12, wherein the at least one Fe organometallic precursor is iron pentacarbonyl ($\text{Fe}(\text{CO})_5$).
14. The process according to claim 1, wherein the at least one precursor of one metal is of Pd and the at least one precursor of another metal is of Ni.
15. The process according to claim 14, wherein the ratio between the two precursors is between 1:1 and 1:10 or between 1:1 and 10:1 Pd:Ni %w/w.
16. The process according to claim 1, wherein the catalyst is supported on a support material selected from carbonaceous materials, carbon nanomaterials and carbon allotropes.
17. The process according to claim 16, wherein the carbonaceous material is selected from activated carbon, graphite and graphitized materials, glass-like carbons, carbon black, carbon nanotubes, carbon nanofibers, graphene, few-layer graphene and fullerenes.
18. The process according to claim 1, wherein the catalyst is supported on a metallic support comprising or consisting a metal selected from Ag, Ni, Cu, Pd, Ru, Mo and Co.
19. The process according to any one of the preceding claims, wherein each of the at least one precursor materials is added sequentially dissolved in at least one solvent and reacted with another of said at least one precursor materials to afford the multimetallic catalyst.
20. The process according to claim 19, wherein the at least one solvent is an organic solvent, optionally selected from toluene, mesitylene, anisole, benzyl alcohol, alkyl alcohols and alkyl ethers.
21. The process according to claim 19, wherein a palladium organometallic compound selected from bis(dibenzylideneacetone)palladium(0), $(\text{Pd}(\text{dba})_2)$ and $\text{Pd}_2(\text{dba})_3$ is reacted in one-pot with $\text{Ni}(\text{COD})_2$ to form a bimetallic catalyst being an alloy or core-shell catalyst.
22. The process according to claim 19, carried in the presence of a carbon support selected from carbon black, carbon nanotubes and graphene.
23. The process according to claim 1, wherein the catalyst is in a dispersed form.
24. The process according to claim 1, for fabricating nanoparticles of NiPd catalyst material, having a diameter of between 4.0-4.5 nm.

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25. The process according to claim 1, wherein the catalyst is selected from FePd, NiPd and CoPd, each being optionally supported.
26. The process according to any one of the preceding claims, carried out at room temperature or at a temperature higher than 70°C.
27. The process according to claim 1, carried at a temperature above 70°C, above 80°C, above 90°C, above 100°C, above 110°C, above 120°C, above 130°C, above 140°C, above 150°C or above 160°C.
28. The process according to claim 26 or 27, wherein the temperature is above 70°C and below 250°C.
29. The process according to any one of the preceding claims, carried out under microwave radiation.
30. The process according to claim 29, carried out at room temperature.
31. The process according to claim 29, carried out at a temperature above 70°C.
32. A multimetallic catalyst prepared according to the process of any one of claims 1 to 31.
33. Use of a multimetallic catalyst according to claim 32 as an anode catalyst.
34. The use according to claim 33, for use as hydrogen oxidation reaction (HOR) catalyst.
35. An anode catalyst for alkaline HOR, the catalyst being a catalyst according to claim 32.
36. The anode catalyst according to claim 35, wherein the catalytically active metal is palladium (Pd).
37. The anode catalyst according to claim 35, wherein the catalytically inactive metal is Ni, Fe or Co.
38. A catalyst according to claim 32, being a carbon-supported selected from:
 - C:Ni:Pd; in relative amounts: 60:12:28; and a Ni:Pd ratio of 30:70;
 - C:Ni:Pd; in relative amounts: 50:15:35; and a Ni:Pd ratio of 30:70;
 - C:Ni:Pd; in relative amounts: 60:28:12; and a Ni:Pd ratio of 70:30; and
 - C:Ni:Pd; in relative amounts: 50:35:15; and a Ni:Pd ratio of 70:30.
39. The catalyst according to claim 38, being an anode catalyst.



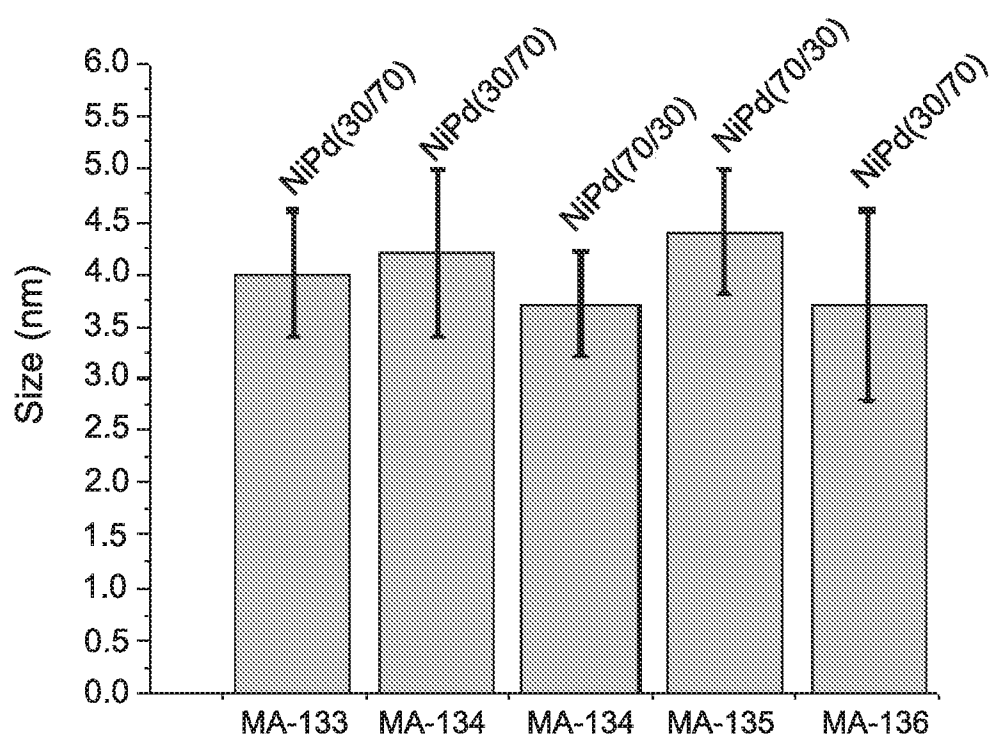
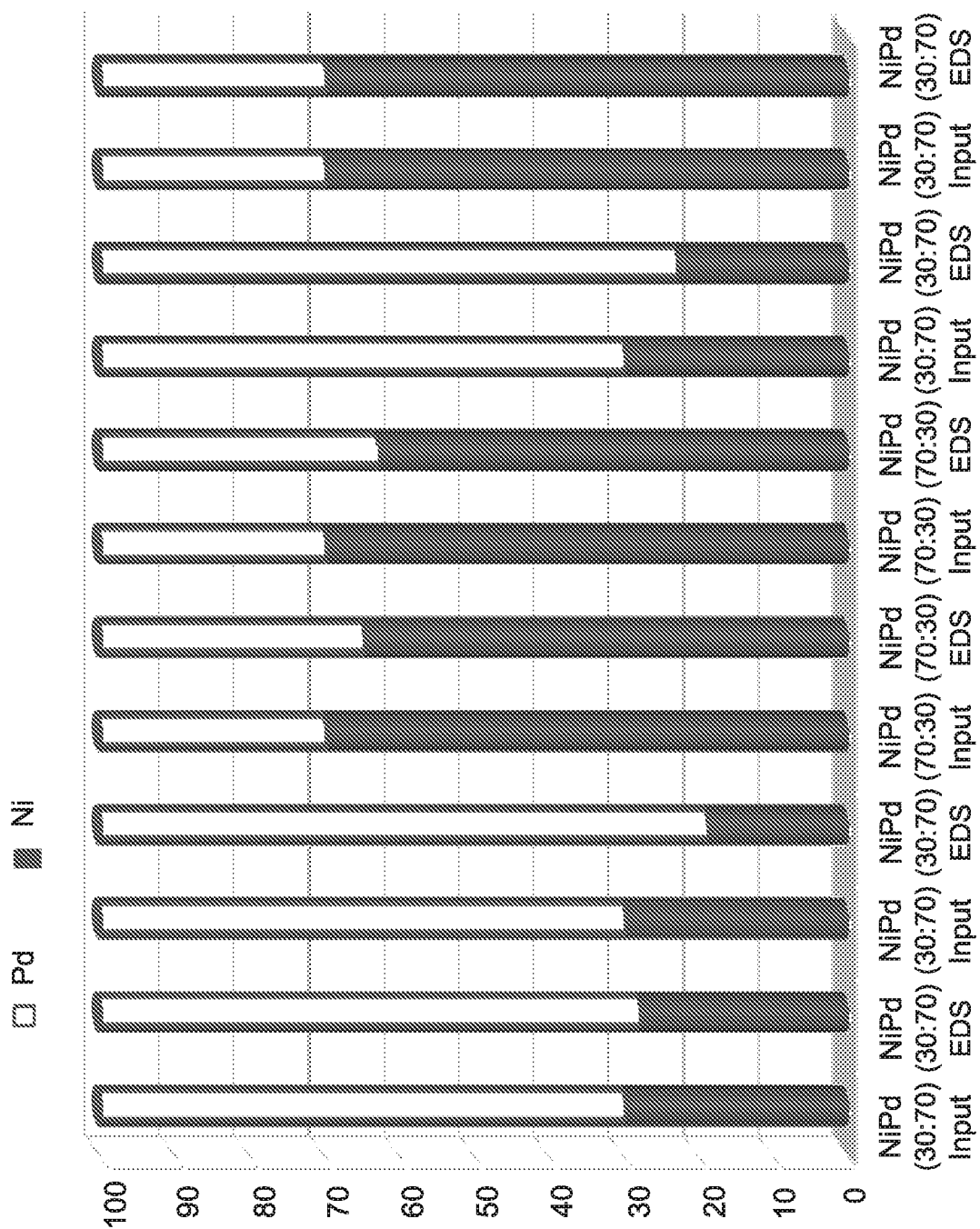


Fig. 2



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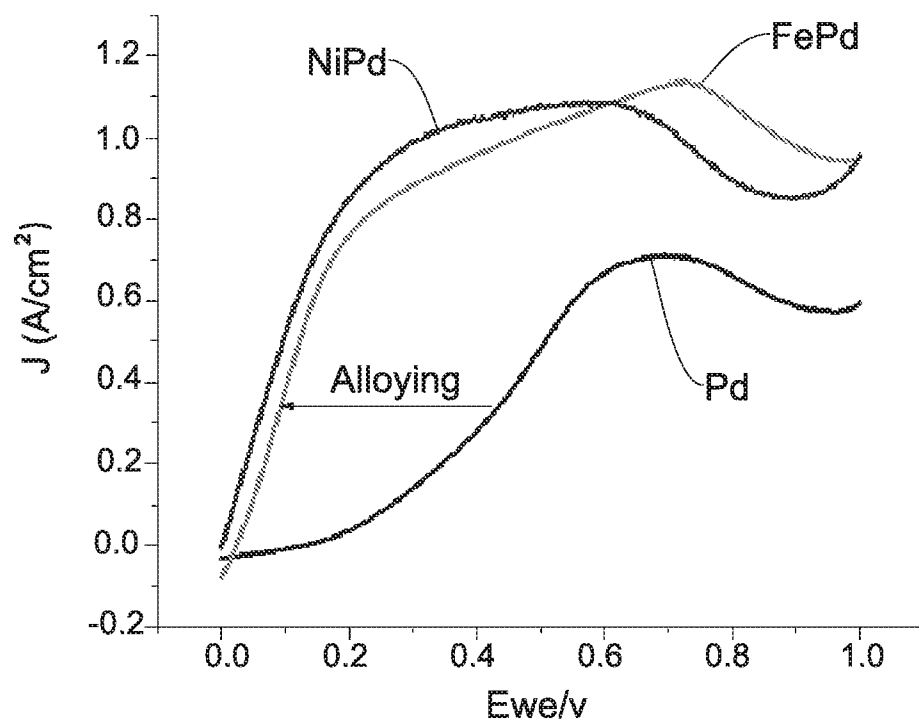


Fig. 4

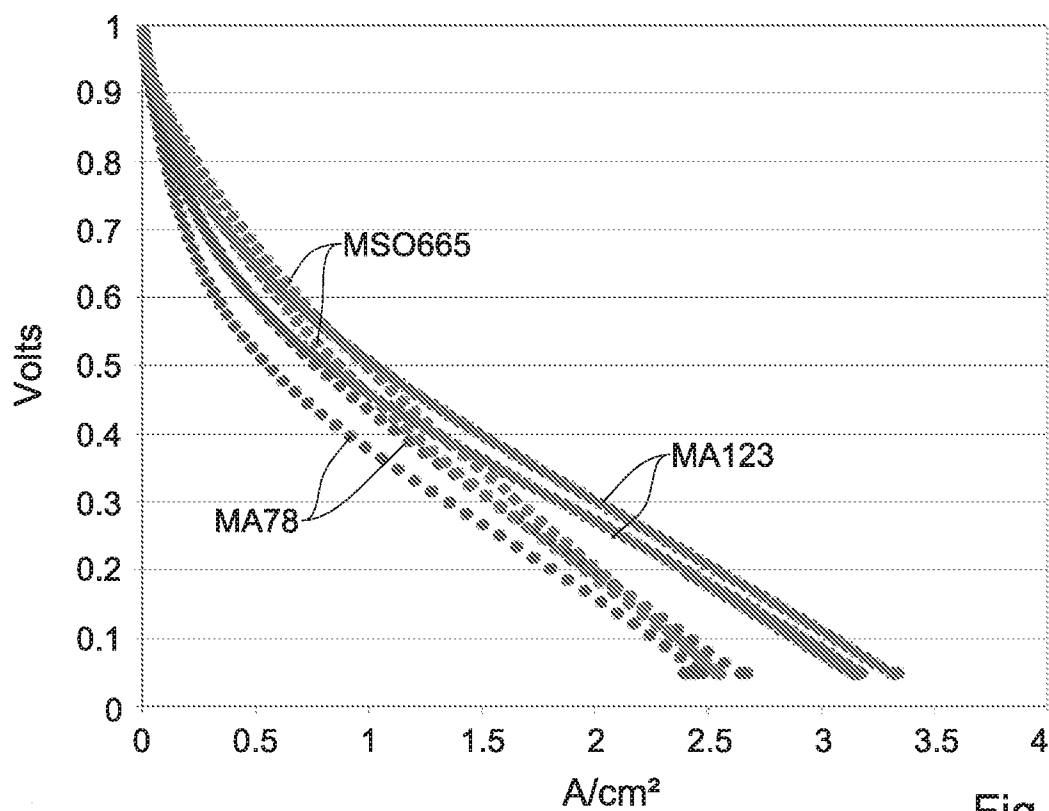


Fig. 5A

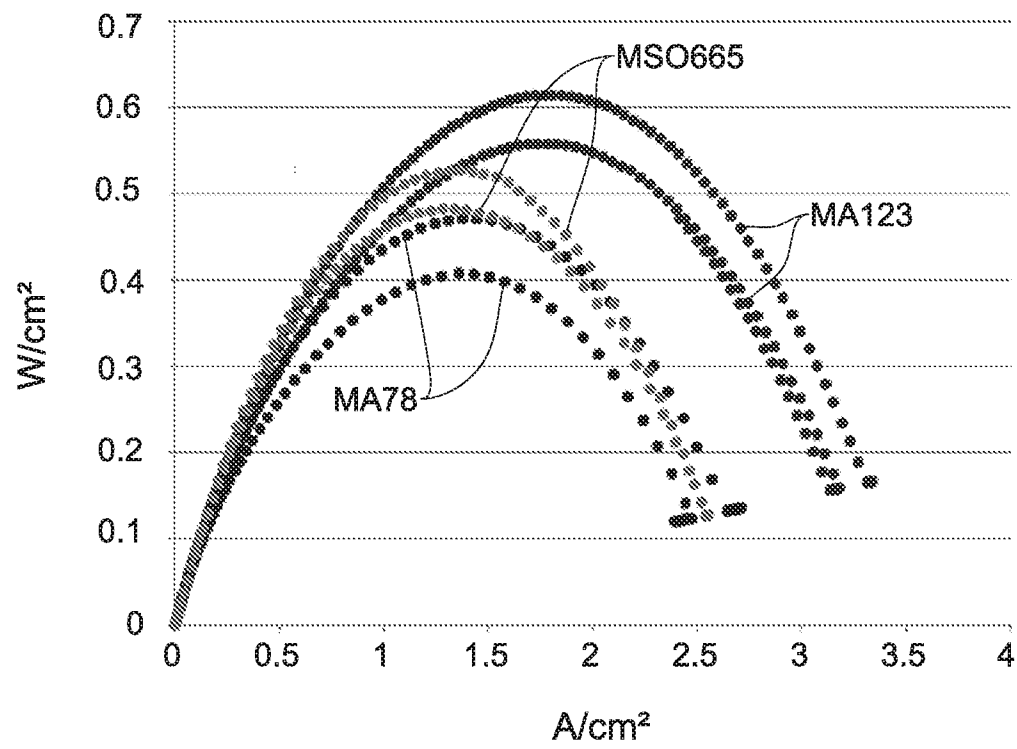


Fig. 5B

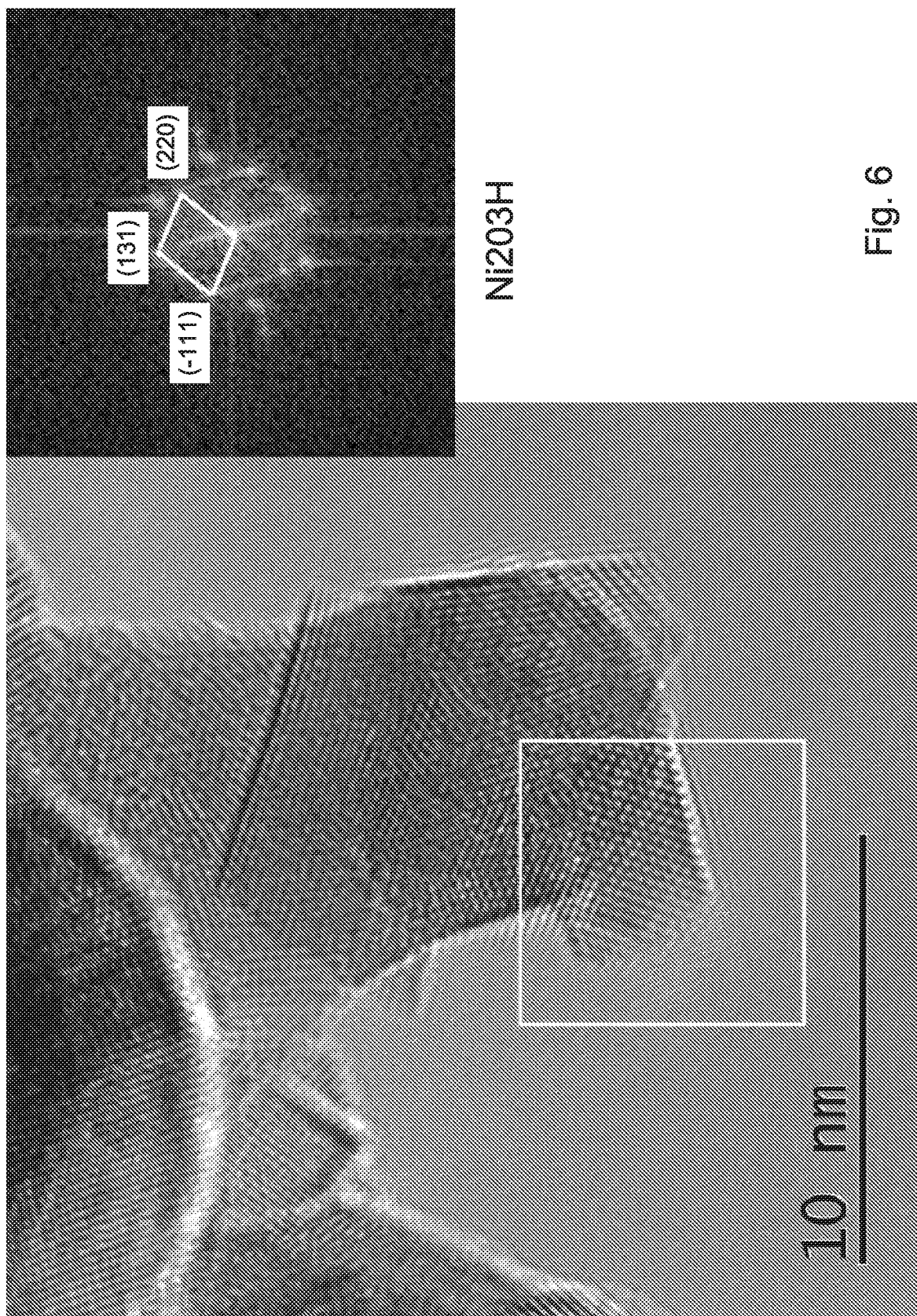


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER IPC (2018.01) B01J 23/40, B01J 37/00, B01J 35/00, B82Y 30/00 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC (2018.01) B01J 23/40, B01J 37/00, B01J 35/00, B82Y 30/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Databases consulted: Esp@cenet, Google Patents, Google Scholar, PatBase Search terms used: Preparation; multimetallic; nanocatalyst; organometallic; precursor		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	US 2011257006 A1 UNIV CLAUDE BERNARD LYON [FR] 20 Oct 2011 (2011/10/20) the whole document	1-39
X	COSTA, Natalia JS, et al. Organometallic preparation of Ni, Pd, and NiPd nanoparticles for the design of supported nanocatalysts. ACS Catalysis, 2014, 4.6: 1735-1742. 14 Apr 2014 (2014/04/14) the whole document	1-39
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 21 Oct 2018		Date of mailing of the international search report 21 Oct 2018
Name and mailing address of the ISA: Israel Patent Office Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel Facsimile No. 972-2-5651616		Authorized officer KATZ Nina Telephone No. 972-2-5651779

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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